Electronic Supplementary Material

Thorium/uranium mixed oxide nanocrystals: Synthesis, structural characterization and magnetic properties

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Supporting information to DOI 10.1007/s12274-013-0379-6

Purification of $Th(acac)_4$. Commercial $Th(acac)_4$ was first dried at room temperature under vacuum for 24 h (mass loss 30%). Then, the dried $Th(acac)_4$ was extracted and crystallized from pentane. After 24 h, big colourless crystals were obtained. The crystals were recovered by filtration, dried at room temperature under vacuum for 24 h and further dried for 4 h at 50 ˚C under vacuum. The final yield was 50%. The crystals were characterized by FTIR and single crystal X-ray diffraction.

Synthesis of $UO_2(OAc)_2{\cdot}2H_2O$. Uranyl acetate $UO_2(OAc)_2{\cdot}2H_2O$ was prepared as described by Grigor'ev and co-workers (*Radiochemistry* **2004**, *46*, 224–231). Briefly, UO_3 was dissolved in a small excess of acetic acid. The solution was stored at room temperature for a day. The obtained precipitate was filtered under vacuum, washed with deionized water and dried under air. Its composition was checked by PXRD and thermogravimetric analysis.

Table S1 Starting composition of the various reaction mixtures used to prepare the stock solutions dedicated to the controlled hot co-injection

Sample	$Th(acac)_4$ (mmol)	$UO_2(OAc)_2{\cdot}2H_2O$ (mmol)	BnOBn[a] (mmol)	OA (mmol)	$N(Oct)_3$ (mmol)	$OP(Oct)_3$ (mmol)
MOX-1	0.3	0	20	0.57	2.87	2.86
MOX-2	0.29	0.01	19	0.60	3.02	3.02
MOX-3	0.22	0.02	16	0.50	2.48	2.48
MOX-4	0.22	0.05	19	0.63	3.16	3.16
MOX-5	0.16	0.16	19	0.64	3.19	3.21
MOX-6	0.15	0.39	31	1.04	5.22	5.25
MOX-7	0	0.32	19	0.64	3.19	3.19

[a] Concerning BnOBn, only half of the quantity reported in Table S1 was used to prepare the corresponding stock solution. The other half was used as a solvent in which the stock solution was slowly injected (i.e., controlled hot injection).

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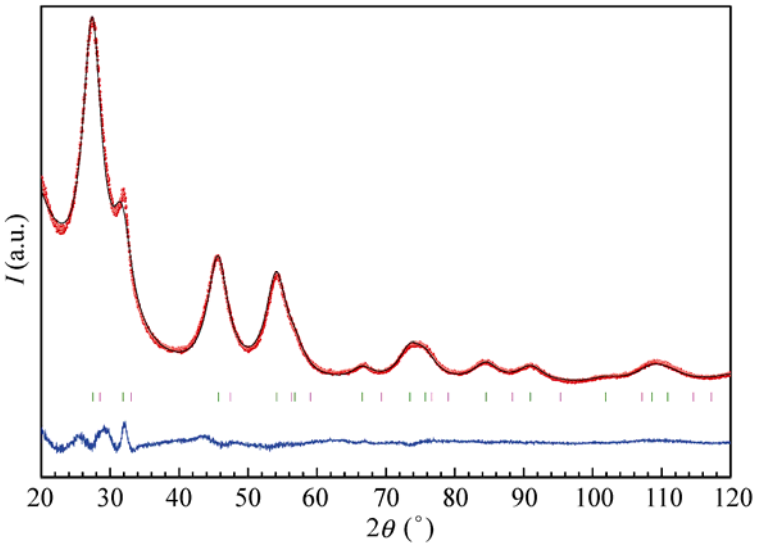

Figure S1 Rietveld refinement of room temperature PXRD data of the MOX-1 sample (starting thorium/uranium molar content: 100/0). The synthesis was performed by the controlled hot injection in BnOBn (T = 260 °C) of $Th(acac)_4$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). Data points are shown (red spheres) with the fit (black solid line) and the difference curve (blue solid line). Tick marks indicate bulk thorium dioxide (green) and uranium dioxide (magenta) Bragg peak positions.

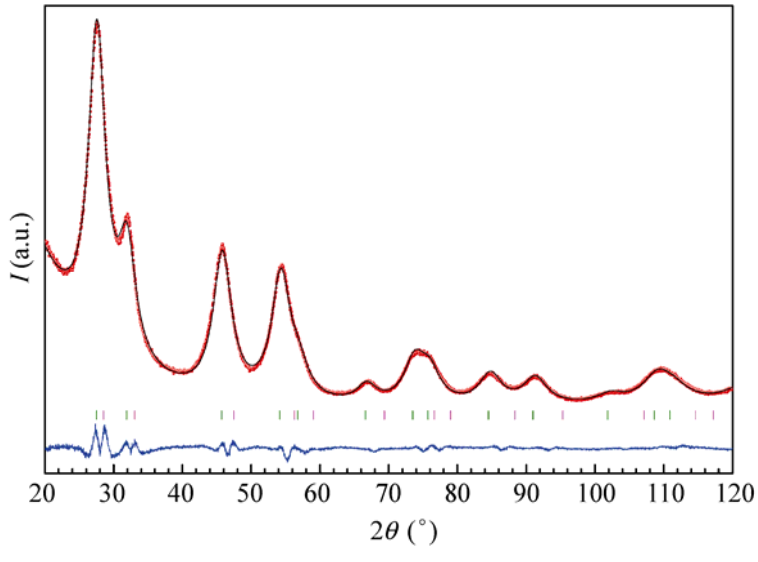

Figure S2 Rietveld refinement of room temperature PXRD data of the MOX-2 sample (starting thorium/uranium molar content: 95.5/4.5). The synthesis was performed by the controlled hot injection in BnOBn (T = 260 °C) of $Th(acac)_4$ and $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). Data points are shown (red spheres) with the fit (black solid line) and the difference curve (blue solid line). Tick marks indicate bulk thorium dioxide (green) and uranium dioxide (magenta) Bragg peak positions.

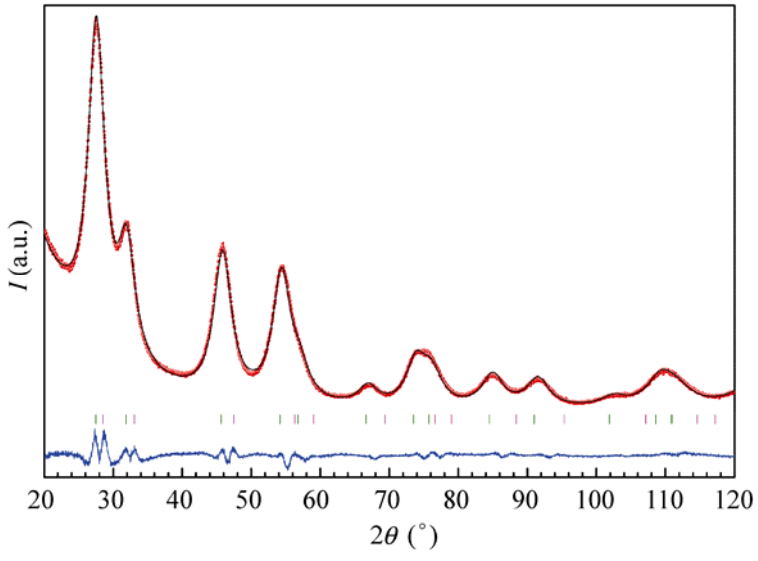

Figure S3 Rietveld refinement of room temperature PXRD data of the MOX-3 sample (starting thorium/uranium molar content: 90.5/9.5). The synthesis was performed by the controlled hot injection in BnOBn (T = 260 °C) of $Th(acac)_4$ and $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). Data points are shown (red spheres) with the fit (black solid line) and the difference curve (blue solid line). Tick marks indicate bulk thorium dioxide (green) and uranium dioxide (magenta) Bragg peak positions.

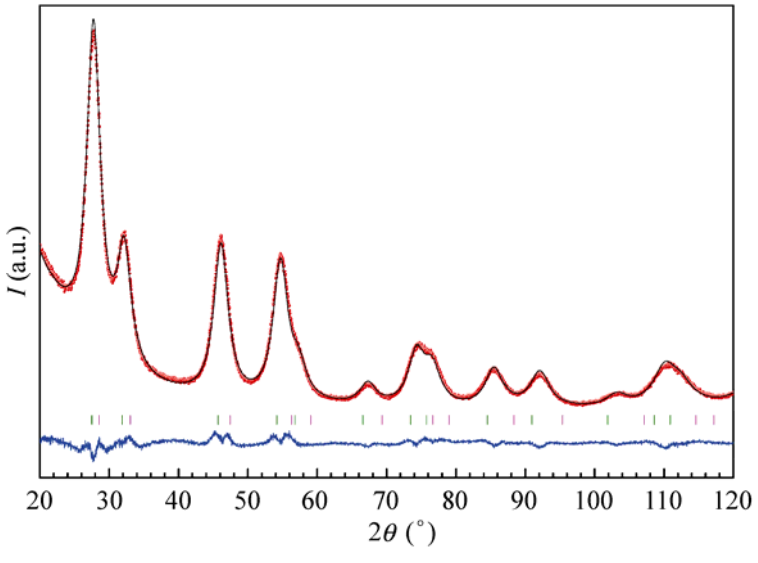

Figure S4 Rietveld refinement of room temperature PXRD data of the MOX-4 sample (starting thorium/uranium molar content: 81/19). The synthesis was performed by the controlled hot co-injection in BnOBn (T = 260 °C) of $Th(acac)_4$ and $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). Data points are shown (red spheres) with the fit (black solid line) and the difference curve (blue solid line). Tick marks indicate bulk thorium dioxide (green) and uranium dioxide (magenta) Bragg peak positions.

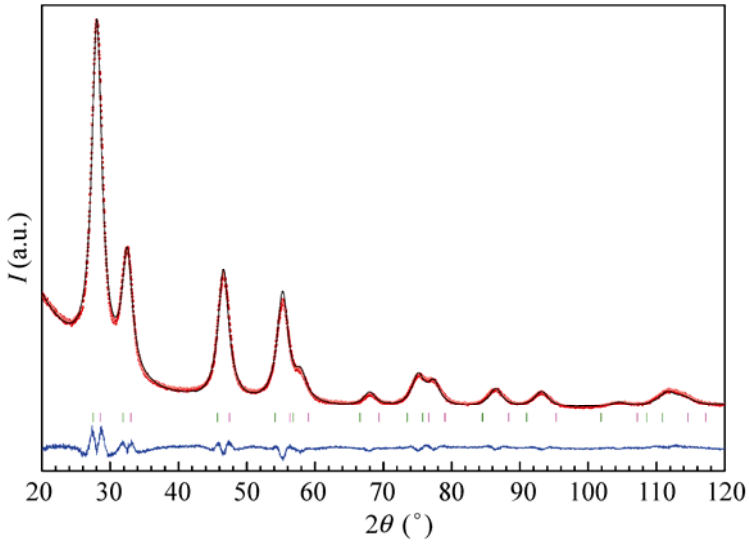

Figure S5 Rietveld refinement of room temperature PXRD data of the MOX-5 sample (starting thorium/uranium molar content: 50/50). The synthesis was performed by the controlled hot co-injection in BnOBn (T = 260 °C) of $Th(acac)_4$ and $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). Data points are shown (red spheres) with the fit (black solid line) and the difference curve (blue solid line). Tick marks indicate bulk thorium dioxide (green) and uranium dioxide (magenta) Bragg peak positions.

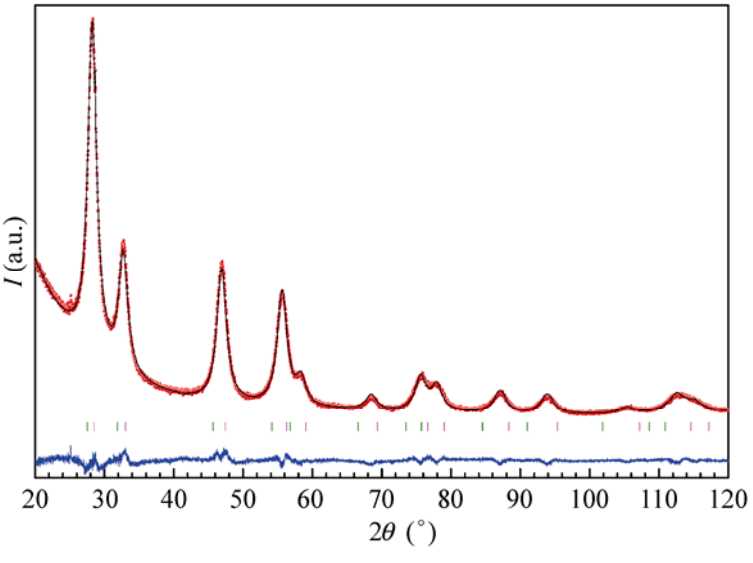

Figure S6 Rietveld refinement of room temperature PXRD data of the MOX-6 sample (starting thorium/uranium molar content: 28/72). The synthesis was performed by the controlled hot co-injection in BnOBn (T = 260 °C) of $Th(acac)_4$ and $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). Data points are shown (red spheres) with the fit (black solid line) and the difference curve (blue solid line). Tick marks indicate bulk thorium dioxide (green) and uranium dioxide (magenta) Bragg peak positions.

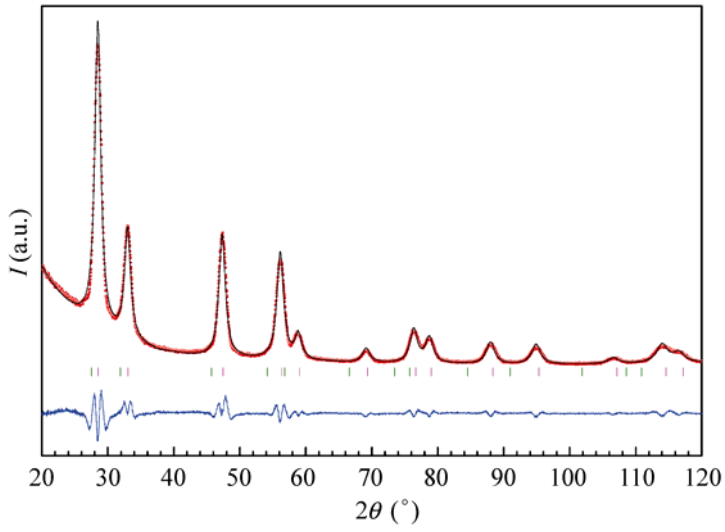

Figure S7 Rietveld refinement of room temperature PXRD data of the MOX-7 sample (starting thorium/uranium molar content: 0/100). The synthesis was performed by the controlled hot injection in BnOBn (T = 260 °C) of $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). Data points are shown (red spheres) with the fit (black solid line) and the difference curve (blue solid line). Tick marks indicate bulk thorium dioxide (green) and uranium dioxide (magenta) Bragg peak positions.

Table S2 Final results of the Rietveld refinements of various thorium/uranium mixed oxide nanocrystals. The syntheses were performed by the controlled hot co-injection in BnOBn (T = 260 °C) of $Th(acac)_4$ and $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). The lattice parameters, crystallite sizes and isotropic atomic displacement parameters as well as the values of reliability (R_p, R_{wp} and GOF) are given

	MOX-1	MOX-2	MOX-3	MOX-4	MOX-5	MOX-6	MOX-7
a (Å)	5.6073 (8)	5.5953 (4)	5.5833 (4)	5.5584 (4)	5.5113 (4)	5.4796 (3)	5.4346 (3)
V (Å^3)	176.30 (2)	175.172 (13)	174.047 (12)	171.732 (11)	167.403 (13)	164.535 (9)	160.508 (10)
C_{size} (nm)	2.7	3.0	3.1	3.9	5.1	5.9	8.4
U_{iso} (An*) (Å^2)	0.0273 (2)	0.01526 (13)	0.01255 (13)	0.0180 (12)	0.0334 (2)	0.02477 (16)	0.0213 (2)
U_{iso}(O) (Å^2)	0.042 (2)	0.0153 (11)	0.0126 (11)	0.01622 (14)	0.058 (2)	0.0365 (16)	0.045 (3)
R_p	3.14	2.38	2.39	2.89	3.44	3.25	5.15
R_{wp}	3.95	3.04	3.09	3.68	4.34	4.25	6.62
GOF	2.11	1.95	1.91	2.06	2.34	1.64	3.17

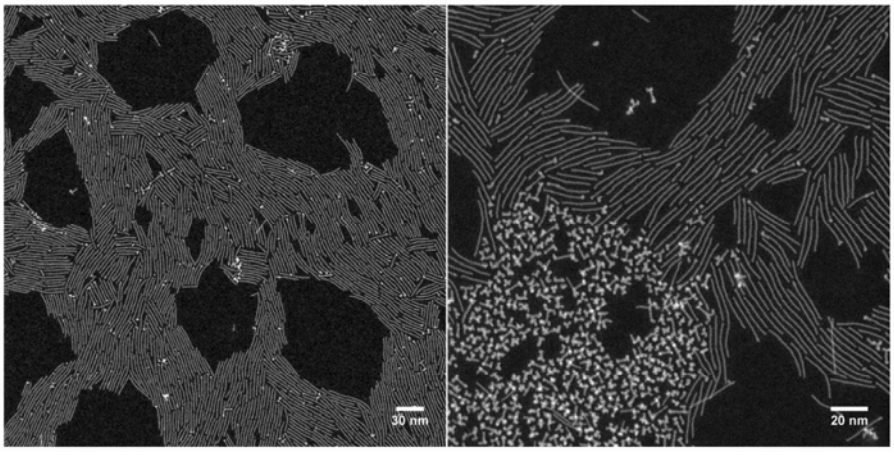

Figure S8 STEM images of pure thorium oxide nanocrystals (MOX-1 sample) synthesized by the controlled hot injection in BnOBn (T = 260 °C) of $Th(acac)_4$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). The left panel shows a low magnification of highly monodisperse thorium oxide nanowires. The right panel shows a mixture of thorium oxide nanowires and dog-bone like nanocrystals.

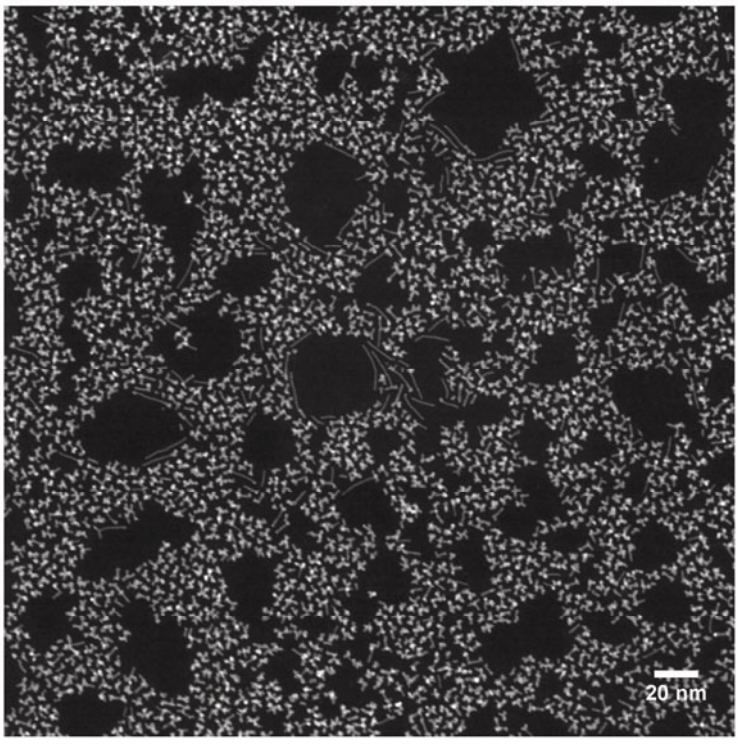

Figure S9 STEM image of thorium/uranium mixed oxide nanocrystals (MOX-2 sample) synthesized by the controlled hot co-injection in BnOBn (T = 260 °C) of $Th(acac)_4$ and $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). The starting composition was: 95.5 mol.% Th/4.5 mol.% U.

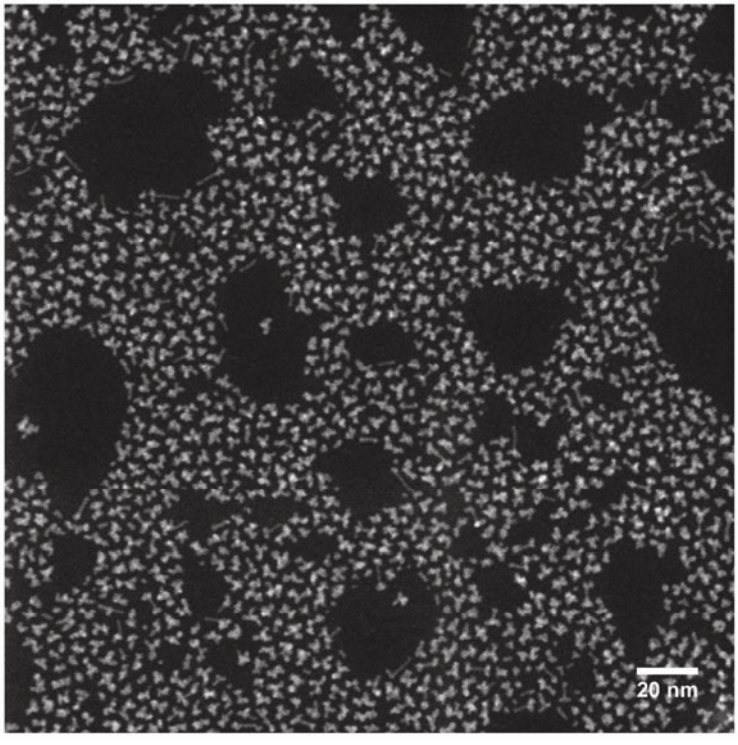

Figure S10 STEM image of thorium/uranium mixed oxide nanocrystals (MOX-3 sample) synthesized by the controlled hot co-injection in BnOBn (T = 260 °C) of $Th(acac)_4$ and $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). The starting composition was: 90.5 mol.% Th/9.5 mol.% U.

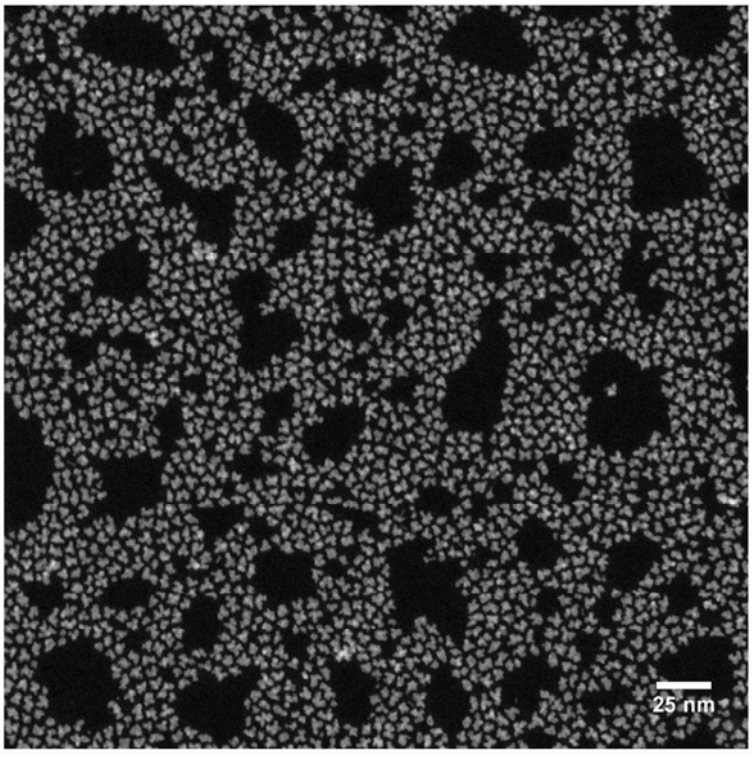

Figure S11 STEM image of thorium/uranium mixed oxide nanocrystals (MOX-4 sample) synthesized by the controlled hot co-injection in BnOBn (T = 260 °C) of $Th(acac)_4$ and $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). The starting composition was: 81 mol.% Th/19 mol.% U.

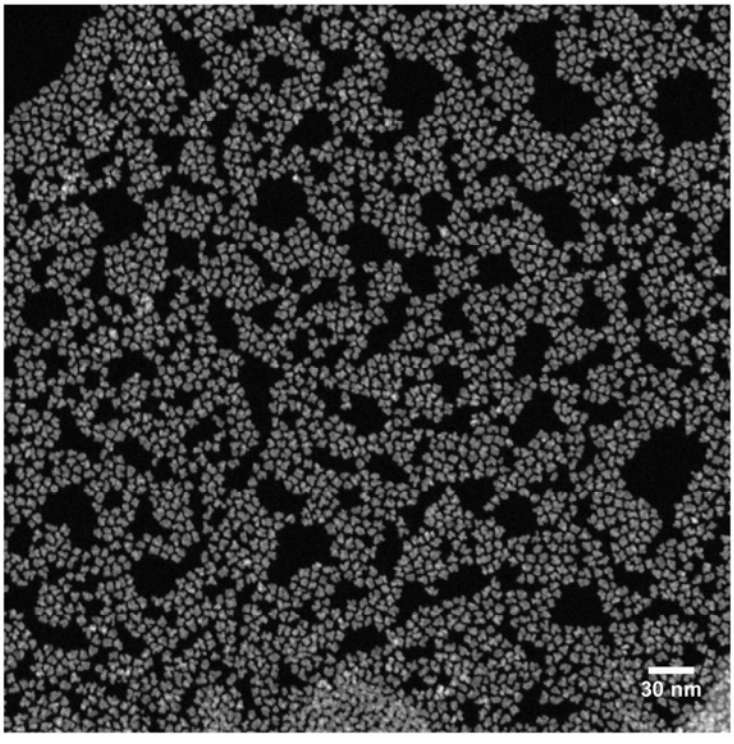

Figure S12 STEM image of thorium/uranium mixed oxide nanocrystals (MOX-5 sample) synthesized by the controlled hot co-injection in BnOBn (T = 260 °C) of $Th(acac)_4$ and $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). The starting composition was: 50 mol.% Th/50 mol.% U.

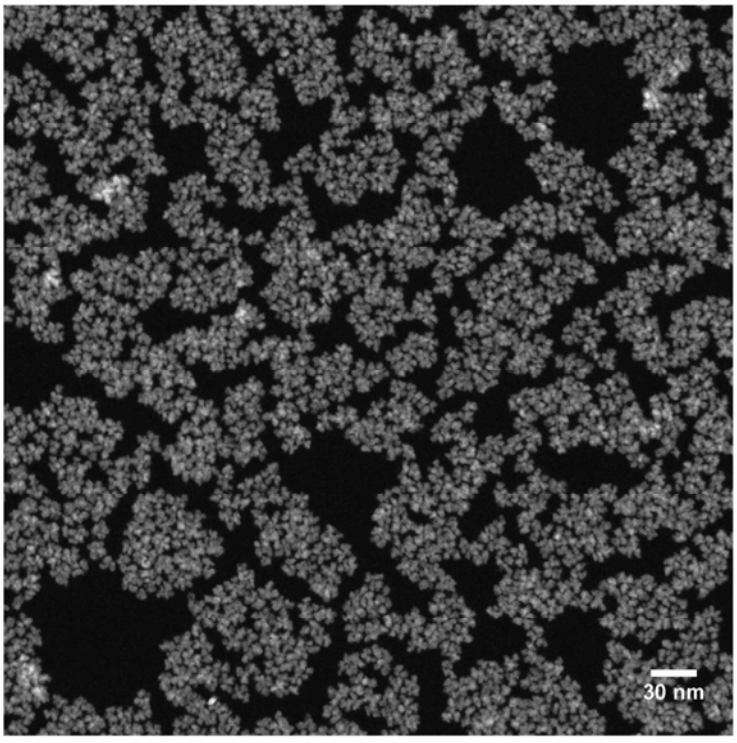

Figure S13 STEM image of thorium/uranium mixed oxide nanocrystals (MOX-6 sample) synthesized by the controlled hot co-injection in BnOBn (T = 260 °C) of $Th(acac)_4$ and $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT). The starting composition was 28 mol.% Th/72 mol.% U.

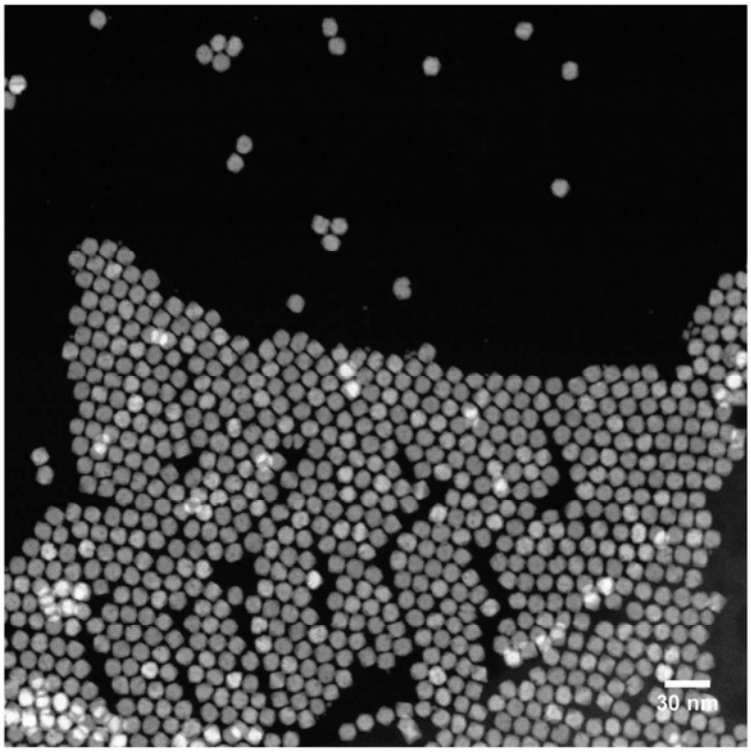

Figure S14 STEM image of pure uranium oxide nanocrystals (MOX-7 sample) synthesized by the controlled hot injection in BnOBn (T = 260 °C) of $UO_2(OAc)_4{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT).

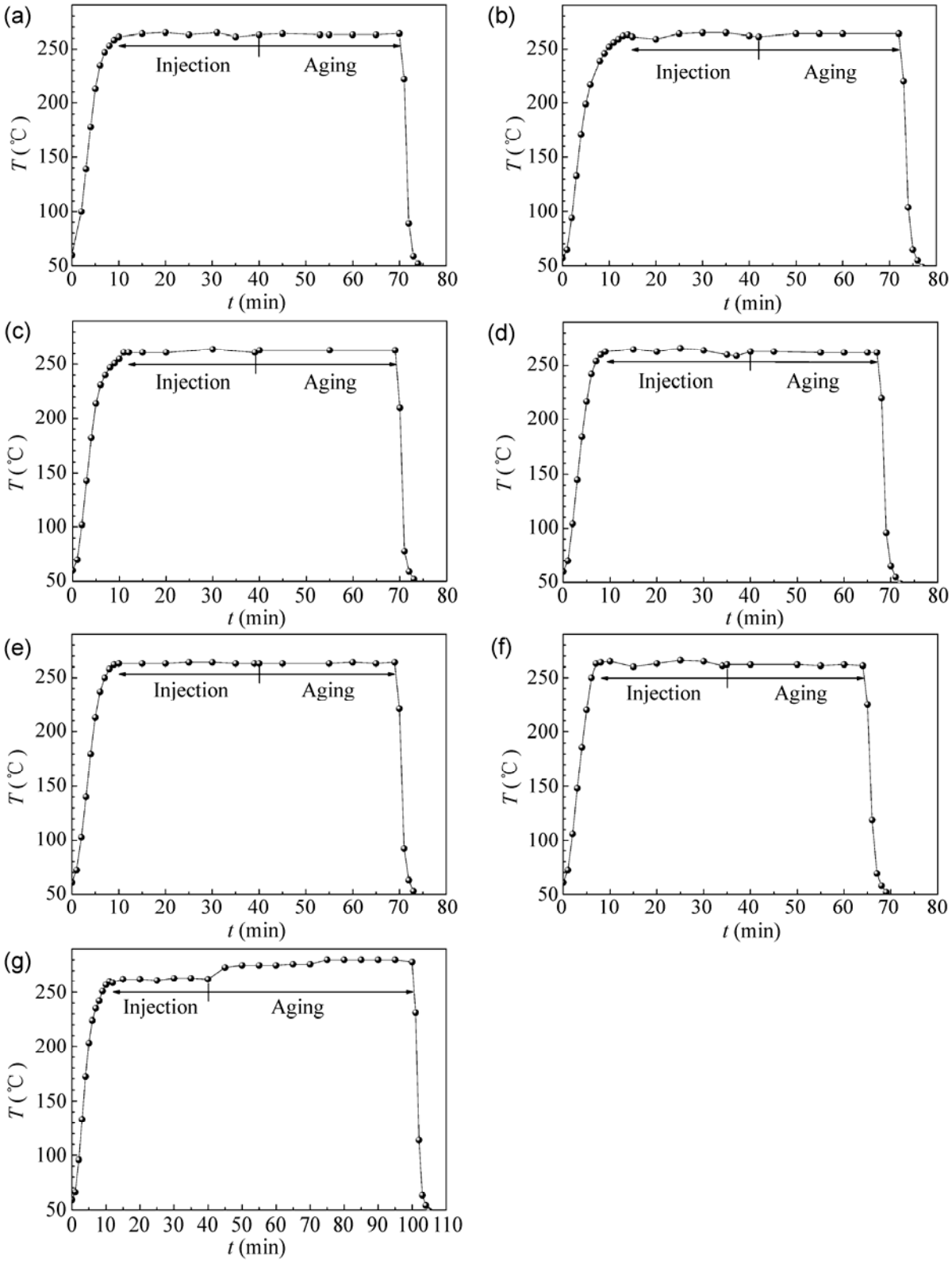

Figure S15 Experimental thermal profiles applied for various MOX samples starting with various thorium/uranium molar contents: (a) 100/0 (MOX-1), (b) 95.5/4.5 (MOX-2), (c) 90.5/9.5 (MOX-3), (d) 81/19 (MOX-4), (e) 50/50 (MOX-5), (f) 28/72 (MOX-6), (g) 0/100 (MOX-7). The syntheses were performed by the controlled hot co-injection in BnOBn (T = 260 °C) of $Th(acac)_4$ and $UO_2(OAc)_2{\cdot}2H_2O$ dissolved in a mixture of OA, $N(Oct)_3$, $OP(Oct)_3$ and BnOBn (RT).